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Thermal Treatment of Raw and Pre-treated Wastes from the Paper Industry

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In this study, the thermal treatment of two types of waste from the paper industry was investigated, paper mill sludge and sewage sludge from biological wastewater treatment plants. Hydrothermal carbonisation (HTC) and torrefaction were investigated as sustainable alternatives for solid biofuel production. Untreated samples and samples chemically pre-treated with alcoholic vinegar were subjected to torrefaction at 350 °C in N_2 atmosphere, and the exhaust gases were analysed. HTC was performed at 250 °C with a residence time of 4 h. The feedstocks and the biochars produced were characterised by different analytical methods, and the effects of pre-treatment on fuel properties were studied. Both processes, HTC and torrefaction, showed inspiring results in the production of biofuels from paper industry wastes under the tested experimental conditions. A positive influence of pre-treatment on fuel properties (higher heating value, carbon content) of the obtained char was observed, and changes in the gas phase during torrefaction were observed.

1. Introduction

The pulp and paper industry generates large amounts of waste, including waste from the production, recycling, and deinking of paper, as well as waste from the treatment of wastewater generated in the paper industry (Reckamp et al., 2014). These materials have the potential to become a renewable source of energy, fuels, and other chemical resources due to their high calorific value and high lignocellulosic content. Current management of waste from the paper industry typically involves incineration and landfilling, both of which are environmental problems due to emissions and pollution (Mendoza Martinez et al., 2021). Various treatment processes can be used to produce biofuels from such wastes. Among thermal treatment processes, pyrolysis, torrefaction, gasification, and hydrothermal treatment have been most studied, although hydrothermal treatment technology is not yet widely used due to various technological challenges. Torrefaction or mild pyrolysis is a thermochemical method to improve the properties of biomass for further energy applications (Orisaleye et al., 2022). The torrefaction process is usually carried out in a temperature range of 200 to 350 °C in an inert atmosphere (Rasam et al., 2020). The main product is solid biochar, which can be used instead of coal. Torrefaction processes have been studied mainly for lignocellulosic biomass such as various wood species or other plants. Non-lignocellulosic biomass such as sewage sludge (Ivanovski et al., 2022) or algae (Barskov et al., 2019) are increasingly coming to the fore. The process itself improves fuel properties by reducing moisture content, increasing high heating value, carbon and oxygen content, and improving grindability (Tian et al., 2020).
HTC treatment has been successfully applied to treat various materials such as agricultural wastes, sewage sludge (Shan et al., 2023), and paper industry wastes (Assis et al., 2021) in the last decade. Since the carbonisation reaction takes place in a liquid medium, drying of the feedstock is not required, which is the main advantage of this process, along with the improved fuel properties of the biomass. The liquid medium used as a reactant in the carbonisation process is usually water, but to improve the properties of the products, it can be replaced by another liquid medium, e.g., whey from the dairy industry (Petrovič et al., 2023) or some other liquid.

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Improving the fuel properties of solid fuels can be achieved by chemically pretreating the feedstocks with certain reagents, such as acids, bases, or other chemicals (Reckamp et al., 2014). There are also some studies on the use of acetic acid (Paiboonudomkarn et al., 2023), citric acid and some other organic acids (Ameen et al., 2022) as catalysts in HTC treatment. However, there is no study on the use of vinegar for such purposes. In this study, wastes from the paper industry were subjected to torrefaction and HTC treatment to produce solid biofuels. In torrefaction, the samples studied were chemically pre-treated with vinegar, while in HTC treatment, vinegar was used as the process liquid instead of conventionally used water.

2. Materials and methods

This section describes material preparation, the process of torrefaction (TOR) and hydrothermal carbonisation (HTC), and methods for characterisation.

2.1 The preparation and characterisation of samples

Wastes from the paper industry were studied, namely paper mill sludge (PM) and biological sludge (BS) from the paper mill wastewater treatment plant. Both samples were dried at 40 °C in a laboratory dryer to constant weight and stored in a desiccator until further use. A portion of the dried samples was pretreated with 9 % alcoholic vinegar obtained by natural acidification and labelled as acidified sludge sample from the paper mill (PMA) and acidified sludge sample from the biological wastewater treatment plant (BSA).
The basic properties of the raw samples and the solid products of TOR and HTC were determined, such as the proximate and ultimate analysis. The higher heating value (HHV) was determined by burning the samples in a bomb calorimeter IKA Isoperibol 6000 according to the standard (SIST-TS CEN/TS 16023:2014, 2014). The ash content was determined as the mass percentage of the residues after the combustion of the samples at 800 °C (3 h). Volatile matter (VM) content was determined by measuring the weight loss after burning the sample at 900 °C (1 h). The elemental analyser PerkinElmer series II 2400 was used to perform ultimate analysis (C, H, N and S content). The process liquids and vinegar were analysed for total nitrogen (TN) and total organic carbon (TOC) content spectrophotometrically using NANOCOLOR cuvette tests (Macherey-Nagel) in addition to conductivity and pH. The properties of the vinegar were as follows: pH = 2.70, conductivity = 1.7 mS/cm, and the content of TOC = 28,700 mg/L.

2.2 The torrefaction process

A pilot process for torrefaction was developed, in which the materials were processed at 350 °C in N_2 atmosphere, and the quality of the biofuel was studied. The schematic of the process is shown in Figure 1.

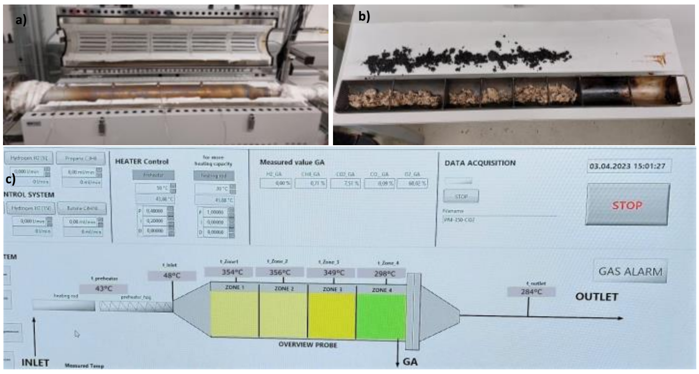

Figure 1: The presentation of the torrefaction process: a) modified Carbolite tube furnace, b) tray for samples and c) process control using SCADA Software Control System

The torrefaction process was carried out in a Carbolite tube furnace with a tube with an inner diameter of 90 mm. The interior of the furnace was adapted to use a tube into which the tray filled with the sample was placed (Figure 1a). Four temperature sensors were attached to the tube to measure the temperature in each zone. Samples were weighed into a special tray (Figure 1b) that had four zones separated by perforated metal. The inlet gas was preheated to 50 °C. Exhaust gases were cleaned through a filter made of propanol and glass wool, and then the concentrations of O_2, H_2, CH_4, CO_2, and CO were measured (Figure 1c). After torrefaction, the samples were weighed again.

2.3 The hydrothermal carbonisation

Hydrothermal carbonisation (HTC) was performed in an autoclave reactor (stainless steel, polyphenylene liner, volume 300 mL) at 250 °C and a residence time of 4 h, with a solid/liquid ratio of 1:6 for biological sludge and 1:8 for paper mill sludge. To investigate the effects of the type of process liquid on the chemical characteristics of the HTC products, two different types of process liquids were used, distilled water and alcoholic vinegar. The reactor containing the reaction mixture was placed in the furnace and heated to a temperature of 250 °C (heating rate of 4 °C/min) and kept at this temperature for another 4 h. The reaction mixture was then cooled and filtered by vacuum filtration. The liquid fraction was stored in a refrigerator. The hydrochar was washed with distilled water, dried at 105 °C and stored for further characterisation.

2.4 Mathematical calculations

To study the effects of thermal treatment on the fuel properties of the samples, the parameters such as mass yield (MY), energy yield (EY), enhancement factor (EF) and energy-mass co-benefit index (EMCI) were calculated using Eqs(1-4) (Ivanovski et al., 2022):

$$\text{MY (\%)} = \frac{\text{mass}_{\text{treated sample}}}{\text{mass}_{\text{raw sample}}} \cdot 100 \quad (1)$$

$$\text{EY (\%)} = \left(\text{MY} \cdot \frac{\text{HHV}_{\text{treated sample}}}{\text{HHV}_{\text{raw sample}}}\right) \quad (2)$$

$$\text{EF} = \frac{\text{HHV}_{\text{treated sample}}}{\text{HHV}_{\text{raw sample}}} \quad (3)$$

$$\text{EMCI} = \text{EY} - \text{MY} \quad (4)$$

Decomposition properties were additionally evaluated by fuel ratio (FR) using Eq(5). The content of fixed carbon (FC) and volatile matter (VM) was determined from the results of the proximate analysis.

$$\text{FR} = \frac{\text{FC}}{\text{VM}} \quad (5)$$

3. Results and discussion

3.1 Characteristics of solid fuel

The basic characteristics of the raw materials and the solid fuels obtained are shown in Table 1. Thermal treatment (torrefaction, HTC) decreased the volatile matter while the ash content increased. The highest increase in ash content was observed in HTC-treated biological sludge, followed by torrefied biological sludge. In contrast to the biological sludge, the torrefied paper mill sludge contained more ash than the HTC-treated sludge. The increase in ash content was due to the volatilisation of organic matter and the accumulation of inorganic matter in the char. In the case of HTC, the organic matter dissolved in the process liquid (Paiboonudomkarn et al., 2023).

The fuel ratio of torrefied biomass was higher than that of raw biomass due to the increased fixed carbon (FC) and lower volatile content. On the other hand, the fuel ratio of HTC-treated biomass was lower due to the lower FC content, as some of the carbon was dissolved in the process fluid. A significant increase in fixed carbon was observed for torrefied biological sludge. The pre-treatment with vinegar increased the fixed carbon content in torrefied samples while replacing water with vinegar in the HTC process had very little effect on FC values.

Elemental analysis showed a significant increase in carbon (C) content in the thermally treated samples and a decrease in oxygen (O) and hydrogen (H) content. The feedstocks (PM and BS) contained about 40 wt.% C, while the thermally treated samples contained between 44.08 and 59.12 wt.%. A higher increase in C content was observed in biochars derived from PM sludge than biochars derived from BS due to the higher volatile content in the first material. A slight increase in C content was also observed in the samples treated with vinegar. The content of sulphur (S) in the treated samples was less than 1 wt.%, except for the torrefied biological sludge (sample T- BS). Biological sludge contained higher concentrations of nitrogen than sludge from paper mills. An interesting behaviour can be observed for the nitrogen content. The TN content increased in paper mill biochars compared to raw samples. On the other hand, hydrothermal carbonisation of biological sludge caused a decrease in N content, while torrefaction of biological sludge caused an increase. This can be explained by the fact that N migrates into the process fluid during HTC treatment, which was also confirmed by the results of the TN measurements of the process liquids.

Higher heating value (HHV) increased after thermal treatment of the samples, particularly biochars of paper mill origin, showed a significant increase in HHV. Interestingly, HTC-treated paper mill samples had higher HHV values than torrefied samples, indicating differences in carbonisation mechanism between the methods used. The HHV values of biochars, derived from biological sludge, were more comparable among themselves. Pre-treatment of the samples with vinegar resulted in an increase in HHV values of the torrefied samples. Similarly, the application of vinegar in the HTC treatment resulted in an increase in HHV levels, indicating the positive effects of vinegar on the carbonisation process. It seems that vinegar acted as a catalyst in the HTC treatment. Similar observations were made when citric or ascorbic acid was used in HTC treatment (Ameen et al., 2022), as an acidic catalyst promotes biomass hydrolysis and dehydration.
The HHV values determined in this study are consistent with those reported in the literature. For HTC treated paper mill sludge, HHV values between 17 and 23 MJ/kg have been reported for paper mill sludge treated with HTC (Assis et al., 2022) and between 21 and 25 MJ/kg for biological sludge (Mendoza Martinez et al., 2021). Similar values (20-23 MJ/kg) were observed for torrefied paper mill sludge (Doddapaneni et al., 2022).

Table 1: The basic characteristics of raw materials and obtained solid fuels.

Sample	Proximate analysis (wt.%)				Elemental analysis (wt.%)					HHV[a] (MJ/kg)	FR[a]
	Moisture	VM[a]	Ash	FC[a]	C	H	N	S	O[b]		
					RAW						
PM	5.35	92.06	5.07	2.86	40.02	6.47	0.80	0.14	47.50	16.2	0.031
PMA	2.85	93.21	3.77	3.03	40.02	6.33	0.67	0.09	49.12	16.6	0.033
BS	2.28	75.77	16.76	7.47	39.85	6.08	6.78	0.90	29.63	17.4	0.099
BSA	1.80	80.41	17.02	2.57	40.70	6.02	6.15	0.09	30.02	18.1	0.032
					TOR 350 °C						
T-PM	4.63	83.54	14.14	2.32	58.22	4.07	1.70	0.20	21.67	19.8	0.028
T-PMA	5.77	77.49	13.27	9.24	59.12	3.64	1.45	0.11	22.41	20.8	0.119
T-BS	2.82	58.86	27.16	13.98	46.68	4.57	7.77	1.08	12.74	20.0	0.238
T-BSA	3.27	47.38	26.43	26.19	48.02	4.71	7.44	0.77	12.63	20.9	0.553
					HTC 250 °C						
H-PM	1.51	89.92	9.29	0.79	54.32	5.63	1.20	0.18	29.38	21.2	0.009
H-PMA	1.60	87.40	10.83	1.77	57.52	5.31	1.47	0.23	24.64	22.4	0.020
H-BS	1.55	66.86	30.84	2.31	44.08	5.39	4.46	0.58	14.65	19.8	0.035
H-BSA	1.64	69.13	28.11	2.76	45.72	5.40	3.94	0.64	16.19	20.4	0.040

[a] VM - volatile mater, FC - fixed carbon, HHV - higher heating value, FR – fuel ratio
[b] Oxygen was calculated using equation: O=100-C-H-N-S-Ash (wt.%)

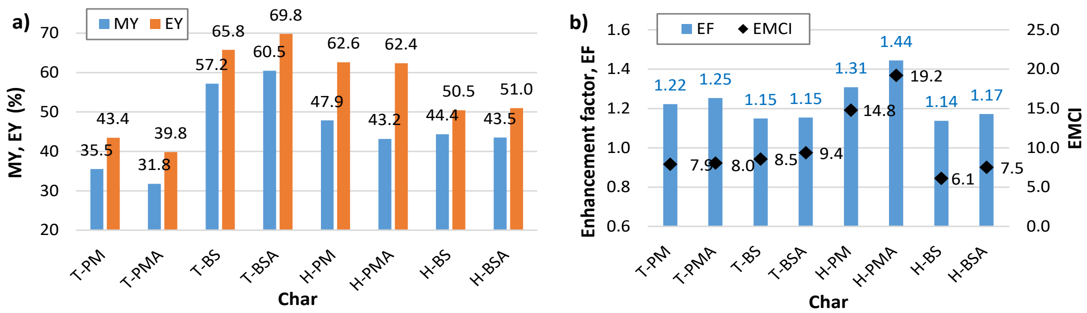

Figure 2: a) Mass yield and energy yield, b) Enhancement factor and energy-mass co-benefit index (EMCI) for obtained biochars

Torrefaction showed better energy and mass yields in the treatment of biological sludge, while HTC gave better results in the treatment of paper mill sludge (Figure 2). The mass yield results followed the same trend as the energy yield. The highest mass yield was calculated for samples T-BSA (60.5 %) and T-BS (57.2 %), slightly lower for samples H-PM and H-PMA (47.9 and 43.2 %), and the lowest for torrefied PM (35.5 %) and PMA (31.8 %). However, it must be considered that the treatment times were not the same. Other studies have reported a wide range of mass yields up to 80 %, depending on feedstock type, composition, and operating conditions (Huang et al., 2017). An enhancement factor reflecting the change in HHV during the torrefaction process was also calculated (Ivanovski et al., 2022). The EF was highest for H-PM and H-PMA, indicating that HHV levels also improved during the torrefaction process. The highest values of the energy-mass co-benefit (EMCI) index were obtained for the materials with the highest EF factor, namely H-PMA and H-PM.

During the torrefaction process, the temperature in three different zones and the composition of the flue gases at the exit were measured. The results for each sample are shown in Figure 3. The temperature was constant during the experiment and fluctuated slightly around 350 °C. From the flue gas analysis, the CO_2 concentration increases the most, especially for sample T-PM, but decreases after a certain time. The time from the increase to the decrease of the CO_2 concentration corresponds to the time during which the torrefaction process takes place in the material. For the samples pretreated with vinegar, the increase in CO_2 concentration was almost negligible, indicating a different chemical composition and reactions during torrefaction. Oxygen present in biomass is released during torrefaction in the form of volatiles, mainly as CO_2, CO, H_2O and partly in other organic compounds such are phenols, acids and ketones (Doddapaneni et al., 2022). This fact explains the high content of CO_2 in the gas phase. The content of other gases was negligible.

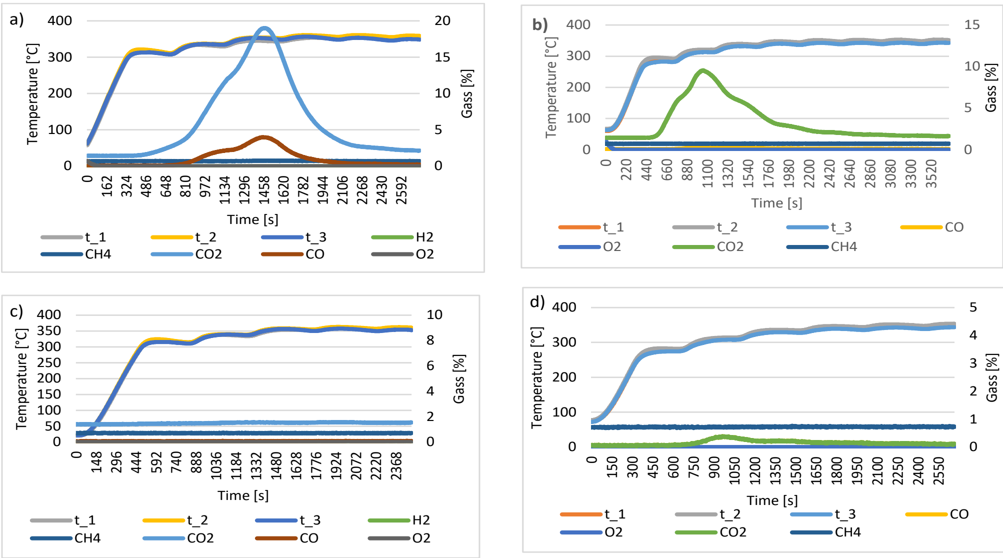

Figure 3: The measurements of temperature and composition of flue gasses during the torrefaction for a) T-PM, b) T-BS, c) T-PMA and d) T-BSA sample

3.2 The properties of the process liquids derived from the HTC process

The pH is one of the most important factors in HTC treatment. The pH of process liquids derived from HTC treatment of biological sludge ranged from 4.35 - 7.7, while lower pH values between 3.1 - 3.4 were measured in the process liquids of paper sludge (Figure 4a). The addition of vinegar resulted in a decrease in pH values, which was more evident in biological sludge. The results of other researchers showed that HTC under acidic medium yields better results (Ameen et al., 2022), which was also confirmed in the present study. The process liquids of the biological sludge had higher conductivity (~19 mS/cm) than the process liquids of the paper mill sludge (~2 mS/cm), which was due to the presence of salts in the biological sludge. Process liquids of the biological sludge, unlike those of the paper mill sludge, were rich in total nitrogen (TN); they contained up to 6,500 mg/L N. High N contents in the process liquids were also found in our previous study on hydrothermal co-carbonisation of municipal sewage sludge and whey, as sludges are known for their high N content (Petrovič et al., 2023). TOC (total organic carbon) values were higher in the process liquids containing vinegar (Figure 4b).

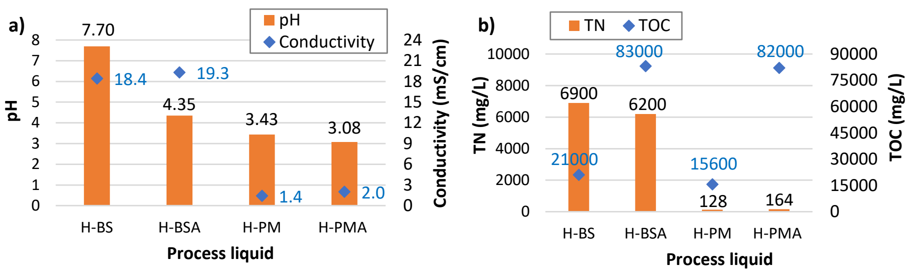

Figure 4: a) pH and conductivity, b) total nitrogen (TN) and total organic carbon (TOC)

4. Conclusions

In this study, solid fuels were produced from paper industry wastes by hydrothermal carbonisation and torrefaction. The methods gave comparable results, although torrefaction showed better results in terms of carbon content. The use of vinegar as a process liquid in HTC treatment and the pre-treatment of biomass with vinegar prior to torrefaction resulted in improved fuel properties of biochars, including an increase in HHV and fixed carbon and lower ash content. Pre-treatment also affects the release of gases during torrefaction. Torrefaction showed higher energy and mass yields when treating biological sludge, while hydrothermal carbonisation gave better results for paper mill sludge. Future work could be directed toward studying the effects of treatment temperature on the chemical properties of vinegar-pretreated solid fuels, as well as the effects of different atmospheres, such as a CO_2 atmosphere, on the torrefaction of chemically pre-treated samples.

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